



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Estrogenic micropollutant adsorption dynamics onto nanofiltration membranes

Citation for published version:

Correia Semiao, A & Schaefer, A 2011, 'Estrogenic micropollutant adsorption dynamics onto nanofiltration membranes', *Journal of Membrane Science*, vol. 381, no. 1-2, pp. 132-141.
<https://doi.org/10.1016/j.memsci.2011.07.031>

Digital Object Identifier (DOI):

[10.1016/j.memsci.2011.07.031](https://doi.org/10.1016/j.memsci.2011.07.031)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Journal of Membrane Science

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Estrogenic micropollutant adsorption dynamics onto nanofiltration membranes

Submitted to Journal of Membrane Science

November 2010

Andrea J. C. Semiao, Andrea I. Schäfer*

School of Engineering, The University of Edinburgh,
Edinburgh, EH9 3JL, United Kingdom

* Corresponding author: Andrea Schäfer, E-mail: Andrea.Schaefer@ed.ac.uk, Phone: +44 (0)131
650 7209, Fax: +44(0) 131 650 6781

Abstract

Nanofiltration (NF) is used in water and wastewater treatment as well as water recycling applications, treating micropollutants such as hormones. Due to their potential health risk it is critical to develop effective treatment processes. Polymeric NF membranes should be effective in removing such micropollutants based on molecular size. However, the occurrence of adsorption onto the membranes results in unpredictable performance. It is hence important to understand NF retention mechanisms.

The focus of this study was to understand how estrone and estradiol adsorption and retention are affected by membrane operational parameters such as pressure, Reynolds numbers (based on channel height Re_h) and feed concentration for the NF270 membrane. These variables are known to contribute to concentration polarisation, and therefore affect sorption and retention by NF membranes.

The total mass adsorbed of both hormones was found to be governed by the initial concentration at the membrane surface. For example, for estradiol the increase of Re_h number (427 to 1450) and pressure (3 to 17 bar) caused the total mass adsorbed to decrease (0.7 to 0.5 ng.cm^{-2}) and increase (0.4 to 0.8 ng.cm^{-2}), respectively. The same trends were obtained for estrone.

Steady-state retention however was found to be dependent on the initial polarisation modulus, given by the ratio between the initial concentration at the membrane surface and the initial feed concentration. For estradiol at the same pressure conditions as above, the polarisation modulus increased from 1.1 to 1.9, causing a decrease of retention from 80% to 51%, whilst for the above Re_h conditions, the polarisation modulus decreased from 1.5 to 1.0 causing an increase in retention from 69% to 83%.

Following on from these results, a model based on a first order sorption kinetics was developed for this membrane allowing the prediction of the transient feed and permeate concentrations for the two hormones estrone and estradiol and a wide range of filtration parameters.

Keywords: Adsorption, estrogen, first order sorption kinetics model, nanofiltration, operational parameters.

1 Introduction

Micropollutants are not fully removed by conventional wastewater treatment processes. Treated wastewater effluents with concentrations up to $\mu\text{g.L}^{-1}$ [1, 2] are discharged into surface waters which raises significant environmental concerns [3, 4]. Estrone and 17- β estradiol are two of the most potent endocrine disrupting contaminants [5-7] and therefore need to be removed from natural and potable water sources. While hormones generally only occur at very low concentrations (ng.L^{-1}) in wastewater effluents [8, 9], concentrations of more than 100 ng.L^{-1} have been measured in US streams [3]. In a UK survey of two rivers [4] an increase in estrone concentration was measured due to the discharge of sewage treatment works, with the estrone concentration profile in one of the rivers clearly following the concentration profile of the plant effluent. Discharge into surface waters of micropollutants, including hormones, poses a health risk to the flora and fauna that depend on these waters [10, 11]. These micropollutants, which have possible negative impact on human health [12, 13], further threaten to contaminate potable water sources.

Nanofiltration (NF) is often installed in water treatment and reuse applications to remove micropollutants. However hormone retention by NF and reverse osmosis (RO) membranes is currently not well understood [14] and is difficult to predict. Retention results from bench-scale studies have been shown to vary significantly for hormones of similar molecular weight, with retentions ranging from 10% to 100% [15]. Some micropollutants, including hormones, pesticides and pharmaceuticals, have been found to adsorb onto NF and RO membranes [14, 16-24]. Such adsorption onto the membrane is highly dependent on the membrane material used [17, 25] and the micropollutant properties such as size, hydrophobicity, acid dissociation constant (pK_a), aptitude for hydrogen bonding [15, 26] and other possible interaction mechanisms [15]. The adsorption phenomenon results in the feed concentration decrease and permeate concentration increase with time, until the membrane is saturated and steady state is reached [14]. This is accompanied by a decrease in the contaminant retention with time until steady-state is reached. Steinle-Darling *et al.* [27] showed that the transient feed concentration and retention of adsorbing perfluorochemicals can be described by a pseudo first-order kinetic equation by fitting the experimental results. This work was very important in furthering the understanding of adsorption of micropollutants onto NF membranes. However, further work is necessary to enable the use of the sorption kinetics in a predictive rather than a descriptive way.

Adsorption of trace contaminants occurring in bench-scale and full-scale applications has several negative implications showing the need to understand the fundamentals of this phenomenon. Firstly, adsorption lowers substantially the retention expected if only steric interactions are considered [14, 28], showing that membrane retention is adsorption dependent. Secondly, adsorption does not occur only in the initial stages of filtration. It has been shown that after each cleaning cycle, adsorbed trace contaminants can be desorbed from the membrane [29, 30], allowing for adsorption to occur again. The adsorption phenomenon is however not understood since studies of adsorbing compounds are usually carried out once the membrane has been pre-saturated with the contaminant [18, 31, 32].

Furthermore, if the study is carried out in a period of time shorter than the required, differing conclusions can be drawn from the results [20, 33]. Whilst a membrane is saturating, the permeate concentration is initially very low, which could lead to the conclusion that the membrane performs well, both in bench-scale [27] and full-scale [34] applications. Bench-scale membrane saturation usually takes a few hours [14, 35] whilst full modules can take more than 4 days [34, 36, 37]. In fact Cornelissen *et al.* [34] did not detect xeno-estrogens in the permeate after 5 days of filtration due to the continuous adsorption onto the membrane module. In the bench-scale study by Steinle-Darling *et al.* [27], no contaminant was detected for 8 hours in the permeate due to adsorption.

The accumulation of contaminants on the polymeric membranes poses a risk since the contaminants can desorb from the membrane during operation or cleaning and contaminate the

permeate [29, 30, 35]. A continuous adsorption-desorption phenomenon can occur during operation caused by fluctuations in feed concentration [30, 35]. For example, if the feed concentration increases, due to fluctuations in the membrane plant inlet, this causes the contaminant adsorption and permeation through the membrane [35].

Trace contaminant removal by NF membranes can therefore be difficult to predict due to the occurrence of adsorption, showing the need in understanding what operation parameters affect it. Understanding the mechanisms involved in the removal of adsorbing trace contaminants by NF membranes at bench-scale will contribute to the understanding of the removal of these in full-scale applications, since the same removal mechanisms are involved.

Several studies have shown that parameters such as feed concentration affect the adsorption of hormones onto NF membranes. Adsorption was found to increase linearly with increasing hormone feed concentration up to 1000 ng.L⁻¹ in filtration mode [38] and up to 600 µg.L⁻¹ in static mode (no pressure applied) [35, 38]. This indicates that adsorption is limited by micropollutant availability. However no studies have been carried out at concentrations close to the hormone solubility limit to confirm that the isotherm is linear for a wide hormone concentration range.

In filtration mode, once adsorption reached steady state and pure water was filtered through the membrane, hormone was released from the membrane into the permeate [35]. Release of hormone on the permeate side can occur if the feed concentration varies. It is therefore important to understand what affects adsorption to be able to control it.

Following the connection between feed conditions and micropollutant adsorption onto NF membranes, another study suggested that feed hydrodynamics affect hormone retention and adsorption [39] but no systematic study on the influence of pressure and Reynolds number (based on channel height Re_h) was carried out. In other studies where different pressures were used [19, 25], membrane saturation was not reached for the studied contaminant. A continuous decrease in the contaminant feed concentration occurred and therefore no conclusions could be drawn on the effect of pressure in the contaminant total mass adsorbed and steady-state retention.

In the work by McCallum et al. [35] the influence of three pressures on the transient feed and permeate concentration of estradiol with the NF 270 membrane was studied. It was shown that pressure has an effect in the transient permeate response: the higher the pressure, the quicker the permeate concentration will reach steady-state. However, the estradiol steady-state feed and permeate concentrations and, therefore, steady-state mass adsorbed and retention, were very similar for the three pressures used, showing no effect of pressure on the hormone retention. In contrast, distinct differences in hormone retention when subjected to different pressures have been obtained elsewhere [40]. In this later study, the authors showed that cross-flow velocity has no effect in estrone retention and that increase of pressure decreases retention. The membranes had been pre-saturated in hormone when carrying out this study and hence, the effect of these parameters on the hormone total mass adsorbed and consequent retention for a virgin membrane were not carried out. As previously mentioned membrane retention is adsorption dependent showing the need to elucidate how filtration parameters affect NF adsorption and retention of trace contaminants.

Due to the clear gap in the understanding of what feed parameters affect adsorption and retention of hormones onto NF membranes, this study will provide a systematic evaluation of the mechanisms that affect these for estrone and 17-β estradiol. Nanofiltration operating conditions, such as pressure and Re_h number will be investigated, as well as feed concentration both in filtration and static mode.

2 Materials and Methods

2.1 Filtration set up

A stainless steel cross-flow system (Figure 1) with a 2.5 L feed tank with a cooling jacket and a high pressure pump (P200 from Hydra-Cell, UK) was used. The system is connected to a flat sheet membrane cell (MMS, Switzerland) with a slit type channel height of 1×10^{-3} m, width of 0.025 m and length of 0.184 m. Temperature was monitored in the retentate by a temperature indicator (WTM Pt 100-0-6 from Condustris-Metag, Germany) and maintained at $24^\circ\text{C} \pm 0.5^\circ\text{C}$ using a cooling jacket with a surface of 0.09 m² connected to a temperature controlled water bath (WK 700, Lauda). A back pressure regulator (KPB1N0A415P60000, Swagelok, UK) allows the pressurization of the system up to 130 bar. The pressure was monitored in both feed and retentate side of the membrane cell with two pressure transducers (S model, Swagelok, UK). The membrane cell holds a membrane of 46 cm². The feed flow was measured using a flow meter (M2SSPI from Hydrasun, UK). Datalogging was set-up allowing for data collection of membrane cell inlet and outlet pressure, feed flow rate and temperature (DAQ 55 Omega, UK). The permeate mass was measured using an Ohaus Adventurer Pro electronic balance (Leicester, UK).

[FIGURE 1]

2.2 Filtration protocol

The filtration protocol used is described as follows. The membrane coupon was gently washed and stored in MilliQ water for at least 12 hours. The membrane was then placed in the cross-flow cell and compacted for two hours with MilliQ water at 25 bar. The pure water flux was measured at 25 bar for at least 30 minutes to ensure steady flux followed by flux measurement at the experimental pressure for ten minutes. The system was then drained of the MilliQ water used and a volume of 1.5 L of fresh MilliQ water was recirculated in the system for one hour at a set hydrodynamic condition by varying pressure (3 to 17 bar) or Re_h number (400 to 1500) to make sure all the process parameters were constant. The Re_h number is given by equation (1),

$$Re_h = \frac{\rho v h}{\mu} \quad (1)$$

where ρ is the solution density (kg.m⁻³), v is the velocity in the feed channel (m.s⁻¹), h is the cell height (m) and μ is the solution viscosity (Pa.s). The Re_h number is adjusted by changing the velocity in the feed channel, hence by varying the feed flow rate. A Re_h number variation between 400 and 1000 corresponds to a feed flow rate variation between 0.55 L.min⁻¹ and 1.37 L.min⁻¹ in the system used in the present study. For NF spiral-wound membranes the realistic operating range for aqueous solutions varies from 3 to 20 bar for pressure [41] and from 100 to 1000 for Re_h numbers [42].

Feed and permeate samples were taken of the MilliQ water to ensure no hormone contamination of the system occurred. The feed tank was then spiked with hormone solution (0.5 L) to reach the required concentration in the system and mixed well using a mechanic stirrer (200 rpm). The feed and permeate concentrations were measured at regular time intervals (every five minutes for the first half hour and then once every hour) to obtain the transient trend until equilibrium was reached (average of 8 hours). The normalized permeate transient flux (J/J_0) is obtained by dividing the permeate transient flux (J , obtained by weighing the amount of permeate mass collected in one minute) by the pure water flux (J_0) measured before spiking the hormones. The system was operated in recirculation mode. New membranes were used for every experiment and membrane samples with a pure water flux of $17 \text{ L.h}^{-1}.\text{m}^2.\text{bar}^{-1} \pm 10\%$ were selected. The transient mass adsorbed was then obtained by mass balance. As a control experiment, adsorption of hormone onto the filtration system in the absence of membrane was investigated. A feed concentration of 100 ng.L⁻¹ of estradiol was recirculated in the system for 8 hours. A difference in

feed concentration of less than 5% was obtained with time showing that for the duration of the experiments, no significant adsorption occurred to the system.

Triplicates of selected experiments at set filtration conditions were carried out and it was found that steady-state retention did not vary by more than $\pm 5\%$, total mass adsorbed by $\pm 0.08 \text{ ng.cm}^{-2}$ and J/J_0 by ± 0.02 .

2.3 Membrane type

The NF270 membrane was used in this study (FilmTec Corp., MN, USA). This high-flux membrane has been found in previous studies to adsorb high quantities of micropollutants, including hormones [14, 27]. It is a thin-film composite (TFC) membrane consisting of a polyamide active layer with polysulfone and polyester support layers. Membrane characteristics can be found in Table 1. The isoelectric point of the membrane was measured with an electrokinetic analyser (EKA, Anton Paar KG, Graz, Austria) in background electrolyte (1mM NaHCO_3 and 20mM NaCl).

[TABLE 1]

2.4 Membrane molecular weight cut-off (MWCO) and salt retention

The nominal MWCO of this membrane is 180 Da (similar to published literature [43]), determined in the cross-flow system at 11 bar and $\text{Re}_h=1450$ using different organics at 25 mgC.L^{-1} , such as dioxane, dextrose (both from Fisher, UK), xylose (Acros Organics, UK) and PEG (400, 600 and 1000 from Fisher UK). The feed and permeate concentrations were measured with a TOC analyser (Shimadzu TOC-VCPH, UK) with an ASI autosampler. Analyses were conducted in non-purgeable organic carbon mode (NPOC) with the high sensitivity catalyst. Comparing the molecular weight of the hormones to the MWCO of the membrane, the hormones would be expected to be retained based on size-exclusion.

NaCl retention was determined in the cross flow system at 10 bar and a Re_h number of 1450, where the feed and permeate conductivity were measured with a pH/Cond 340i meter (WTW, Germany).

2.5 Chemicals and analysis

Radiolabelled hormones were used due to very low detection limit, small sample volumes required and extremely high accuracy. The radiolabelled hormones used were $[2,4,6,7\text{-}^3\text{H}]$ estrone (E1) and $[2,4,6,7\text{-}^3\text{H}]$ 17 β -estradiol (E2) (GE Healthcare and Perkin Elmer, UK, respectively). These two hormones are amongst the most endocrine disrupting chemicals, as previously mentioned, and their chemical properties are found in Table 2.

[TABLE 2]

An initial feed concentration of 100 ng.L^{-1} was used in all the experiments, with the exception of the isotherm experiments where concentrations were varied from 25 ng.L^{-1} to 2 mg.L^{-1} . The radioactivity of the permeate and feed samples were measured using a Beckman LS 6500 scintillation counter (Fullerton, USA), where 0.5 mL of sample was placed in scintillation vials (Perkin Elmer, UK) with 4 mL of Ultima Gold LLT (Perkin Elmer, UK) and counted for 10 minutes each. The detection limit of this method is 1 ng.L^{-1} for the hormones studied. No other chemicals or background salts were used. The feed and permeate pH and conductivity were regularly measured with a pH/Cond 340i meter (WTW, Germany) to ensure stability of these two parameters. The value of pH varied in the feed and permeate by $\text{pH}=6.5\pm 0.75$ and conductivity $\text{Cond}=1 \text{ }\mu\text{S.cm}^{-1}$.

2.6 Isotherm experiments

To achieve the higher concentrations ($>200 \text{ ng.L}^{-1}$) used in isotherm studies, non-labelled hormones ($>98\%$ purity) were obtained from Sigma Aldrich, UK, and mixed with labelled hormones. For the adsorption isotherms of E2 the highest concentration chosen (2 mg.L^{-1}) was close

to the solubility limit (3.6 mg.L^{-1} [18]) to try to reach saturation of all the adsorption sites on the membrane. The E2 adsorption isotherm was determined in filtration mode to see if filtration had any impact on the shape of the isotherm. In addition and to compare with the filtration results, isotherm experiments in static mode in a Certomat BS-1 UHK-25 shaker (Göttingen, Germany) at 200 rpm and 24°C (*i.e.* no pressure applied) with the same feed concentrations were carried out in 60 mL vials of the relevant hormone concentration with pieces of the membrane (45 cm^2 cut into 5 cm^2 pieces).

3 Results and Discussions

Hydrodynamics have a significant impact on membrane retention because they affect the degree with which polarisation develops, and therefore affect the concentration at the membrane surface. The first step in studying the impact of polarisation on hormone adsorption and retention by NF membranes is to be able to calculate the concentration at the membrane surface for the different conditions of pressure, Re_h numbers and feed concentration used.

3.1 Concentration at the membrane surface determination

A concentration gradient forms at the membrane surface due to the accumulation of retained solutes. This concentration gradient creates a diffusive solute flow from the membrane surface to the feed bulk which is counter-balanced by a convective flux towards the membrane surface caused by a pressure difference between the feed side and the permeate side. A balance between these two fluxes and the permeate flux results in the concentration polarisation equation (equation (2)),

$$\frac{C_m - C_p}{C_f - C_p} = \exp\left(\frac{v_p}{k}\right) \quad (2)$$

where C_m , C_p and C_f are the concentrations at the membrane surface, permeate and feed respectively (ng.L^{-1}), v_p is the permeate velocity (m.s^{-1}) and k is the mass transfer coefficient (m.s^{-1}). In the first instances of the experiment, the concentration in the permeate is zero, and equation (2) simplifies to equation (3), the polarisation modulus β [44] at this initial condition. $C_m(0)$ and $C_f(0)$ are the initial membrane and feed concentrations, respectively.

$$\beta = \frac{C_m(0)}{C_f(0)} = \exp\left(\frac{v_p}{k}\right) \quad (3)$$

To calculate the initial concentration at the membrane surface $C_m(0)$ in equation (2) and (3), the parameters were used considering filtration conditions when the hormones were spiked to the feed tank. The permeate concentration $C_p(0)$ is 0, v_p was calculated based on the pure water flux measured before spiking the hormones and $C_f(0)$ was measured in the experiment.

The mass transfer coefficient, k , required to calculate C_m in equation (2) and (3) was obtained by the Sherwood correlation applied for the same hydrodynamic conditions in a slit channel [45] presented in equation (4),

$$\text{Sh} = \frac{k d_h}{D_\infty} = 1.195 \text{Re}_{\text{dh}}^{0.554} \text{Sc}^{0.371} \left(\frac{d_h}{L_{\text{cell}}}\right)^{0.131} = 1.195 \left(\frac{\rho v d_h}{\mu}\right)^{0.554} \left(\frac{\mu}{\rho D_\infty}\right)^{0.371} \left(\frac{d_h}{L_{\text{cell}}}\right)^{0.131} \quad (4)$$

where d_h (m) is the hydraulic diameter ($d_h=2\times h$, where h is the slit channel in m), D_∞ is the hormone solute diffusivity ($\text{m}^2.\text{s}^{-1}$) determined with the Worch equation [46], Re_{dh} is the Reynolds number based on hydraulic diameter given by $\text{Re}_{\text{dh}}=\rho\times v\times d_h/\mu$, Sc is the Schmidt number given by $\text{Sc}=(\mu/(\rho\times D_\infty))$, L_{cell} is the cell length (m), ρ is the solution density (kg.m^{-3}), and μ is the solution viscosity (Pa.s). Due to the very low hormone concentrations, pure water parameters were used.

3.2 Influence of Hydrodynamics: Reynolds number

The effect of Re_h on the total E1 and E2 hormone mass adsorbed (Mass Ads. in Figure 2) and retention at steady-state ($Retention_{ss}$) is shown in Figure 2 A and B. The later is calculated using the feed and permeate concentrations once steady-state is reached.

When Re_h numbers increased from 427 to 1450, the E2 total mass adsorbed decreased from 0.7 ng.cm^{-2} to 0.5 ng.cm^{-2} and the $Retention_{ss}$ increased from 61% to 81%. When Re_h increases, this causes a lower concentration polarisation to form on the membrane surface: hence $C_m(0)$ or β given by equation (3) are lower (Figure 2 C). In fact the increase of Re_h from 427 to 1450 caused the polarisation modulus to decrease from 1.5 to 1.0.

The same trend was obtained for E1, where an increase of Re_h numbers from 427 to 1450 caused the total mass adsorbed to decrease from 1.5 ng.cm^{-2} to 1.3 ng.cm^{-2} and a $Retention_{ss}$ increase from 69% to 83%. This was accompanied by a polarisation modulus decrease from 1.5 to 1.0. Lower $C_m(0)$ or β results in lower adsorption and higher $Retention_{ss}$, showing that adsorption and $Retention_{ss}$ are governed by $C_m(0)$ or β .

[FIGURE 2]

As pressure impacts significantly on concentration polarisation, the contribution of pressure was studied systematically to determine the influence of pressure induced changes in $C_m(0)$ and β on adsorption.

3.3 Influence of Hydrodynamics: Pressure

Results of the role pressure plays on the total mass adsorbed and $Retention_{ss}$ is depicted in Figure 3 A and B. Increasing pressure increased flux (v_p) through the membrane and therefore increased $C_m(0)$ or β (Figure 3 C) as a consequence of polarisation (equation 3). This was accompanied by an increase in the hormone mass adsorbed and a decrease in $Retention_{ss}$, confirming that $C_m(0)$ or β indeed govern adsorption and $Retention_{ss}$. When the pressure increased from 3 to 17 bar, E2 $C_m(0)$ or β almost doubled from 100 ng.L^{-1} to 190 ng.L^{-1} or 1.1 to 1.9, respectively. This caused an increase of the mass adsorbed from 0.4 ng.cm^{-2} to 0.8 ng.cm^{-2} and a decrease of $Retention_{ss}$ from 80% to 51%. The same trend was obtained for E1, where an increase of pressure from 5 to 15 bar caused a mass adsorbed increase from 1.0 ng.cm^{-2} to 1.8 ng.cm^{-2} and a $Retention_{ss}$ decrease from 85% to 63%.

[FIGURE 3]

When comparing Figure 2 and Figure 3, Re_h impacts less on adsorption or $Retention_{ss}$ compared to pressure. This is expected since according to equation (3) and (4) C_m is more sensitive to changes in pressure or permeate velocity (v_p) than to changes in the velocity v in the feed channel (or Re_h number).

Variations in hydrodynamic conditions affect the membrane surface concentration. To elucidate the role of concentration at constant hydrodynamic conditions a systematic study of the effect of feed concentration on adsorption and retention was carried out.

3.4 Feed Concentration Influence on Adsorption

The results of E1 and E2 feed concentration variation on adsorption and $Retention_{ss}$ are presented as adsorption isotherms in Figure 4.

[FIGURE 4]

All hormone isotherms were linear for both filtration and static mode, confirming results of other studies in a lower hormone concentration range [35, 38], showing sorption is limited by the hormone concentration. This suggests that saturation of all the adsorption sites available on the membrane was not reached, not even at the highest E2 concentration (2 mg.L^{-1}). However for this feed concentration, the normalized flux J/J_0 was at least 15% lower compared to the other

concentrations (Figure 5). At these conditions and with a resulting $C_m(0)$ of 3 mg.L^{-1} , the E2 concentration is close to the solubility limit (Table 2), which might cause E2 precipitation and, in consequence, affect membrane performance.

[FIGURE 5]

The total mass adsorbed in Figure 4 increased with increased feed concentration, confirming that it is proportional to $C_m(0)$. However, $Retention_{ss}$ for both hormones was constant. When β was calculated for the isotherm experiments (Figure 4), it was found to be constant for both hormones, with $\beta_{E1} = 1.44 \pm 0.03$ and $\beta_{E2} = 1.49 \pm 0.03$. It can be concluded that whilst the mass adsorbed is dependent on $C_m(0)$, $Retention_{ss}$ is dependent on β .

The reason why the total mass adsorbed and $Retention_{ss}$ depend on $C_m(0)$ and β , respectively, is explained as follows.

Experiments in static mode and filtration mode evidence that a membrane surface exposed to an increasing initial feed concentration of hormone yield an increase of the mass adsorbed (Figure 4). In filtration mode, the total mass adsorbed increases when pressure increases and Re_h decreases (Figure 2 and Figure 3), despite the initial feed concentration being the same for both hormones (100 ng.L^{-1}). Pressure and Re_h number are known to affect the concentration at the membrane surface, hence the conclusion that adsorption and retention are governed by the concentration at the membrane surface.

Experimental data further evidences that the higher the initial concentration at the membrane surface $C_m(0)$ (or β) (Figure 2 and Figure 3), the higher the total mass adsorbed obtained and the lower the retention. This allows one to infer that adsorption and retention are governed by $C_m(0)$ or β , since it is this concentration that the membrane is in contact with in the first instances of the experiment. The previous inference is corroborated by the following observations and reasoning.

If $C_m(0)$ or β did not govern the process of hormone adsorption and retention, then for similar conditions of $C_m(0)$ or β caused by different combinations of Re_h numbers and pressure, different results of total mass adsorbed and $Retention_{ss}$ should be obtained for the hormones. However, as can be seen in Table 3 one can conclude that this is not the case. The same applies for the experimental conditions of 11 bar and 1400 Re_h number, where $\beta=1$, and 5 bar and a 427 Re_h number, where $\beta=1.1$. This shows that for different filtration conditions that lead to the same $C_m(0)$ or β , the same results of steady-state adsorption and retention are obtained, confirming that it is the initial condition that govern the system.

Moreover the use of $C_m(0)$ or β as the governing parameter for the mass adsorbed and retention is an advantage as this allows the latter two to be predicted, as will be described in section 4.

[TABLE 3]

It was further noticed that E1 adsorbs twice as much as E2, which is in agreement with findings of Nghiem *et al.* [14]. Despite having similar physical characteristics [15], hormones with a ketone group (E1) have been found to bind more to organic matter or activated carbon than hormones with a hydroxyl group (E2) [47, 48]. The ketone group in E1 is very electron-rich (or polarised) compared to the hydroxyl group in E2 and therefore forms stronger hydrogen bonding (H-bond), while other interactions, such as hydrophobicity, may be at play as well. Hydrophobicity, however, does not explain the difference in adsorption between E1 and E2 onto NF membranes since despite E2 being more hydrophobic than E1 (Table 2), it adsorbs less.

The main objective in membrane science is to be able to predict the permeate concentration of a certain solute in order to choose the most appropriate membrane to remove it. A model is therefore required, in the first instance for this membrane, to predict the permeate concentration. The above results allowed to do this since the physical mechanisms that influence adsorption, such as the case of polarisation, have now been identified. The model developed predicts the changes in

feed concentration with time which then allow predicting changes in the transient permeate concentration.

4 Sorption Model Development

4.1 Feed concentration prediction

In this study a model that allows prediction of the feed concentration variation with time for a wide range of pressures (3-17 bar) or Re_h numbers (400-1000) has been developed. Assuming pseudo-first-order sorption kinetics for the hormones, equation (5) describes the hormones at equilibrium [49],



where H is the concentration of free hormone ($ng.L^{-1}$), k_1 (s^{-1}) is the pseudo-first order reaction constant and H^* is the adsorbed hormone ($ng.cm^{-2}$).

The differential equation for description of the rate of change of the feed concentration is shown in equation (6), where C_{fss} ($ng.L^{-1}$) is the feed concentration at steady state conditions, t is time (s) and a (s^{-1}) is the rate constant for exponential decline.

$$-\frac{dC_f(t)}{dt} = k_1 (C_f(t) - C_{fss}) \quad (6)$$

Solving equation (6) considering the boundary conditions of $C_f(t) = C_f(0)$ for $t = 0$ one obtains equation (7) [27], where k_1 is dependent on the rate with which the hormone adsorbs onto the membrane surface. This parameter therefore has one value for E1, E2 and the NF270 membrane, and does not depend on experimental conditions.

$$C_f(t) = C_{fss} + (C_f(0) - C_{fss}) e^{-k_1 t} \quad (7)$$

The steady-state concentration C_{fss} will depend on the total mass adsorbed and will therefore vary for different filtration conditions since the mass adsorbed varies with these (as shown in Figure 2, Figure 3 and Figure 4).

The parameter k_1 and C_{fss} need to be determined for using equation (7) in order to predict the feed concentration variation with time. The required information was obtained from the isotherm experiments.

The reaction rate constant k_1 was obtained by fitting equation (7) to the filtration isotherm transient feed concentrations using an optimization method (Solver, Microsoft Excel). For the NF270 membrane $k_1 = 3.00 \times 10^{-4}$ (s^{-1}) for E1 and $k_1 = 3.71 \times 10^{-4}$ (s^{-1}) for E2 were obtained. Since E1 takes longer to reach adsorption steady-state, its reaction rate constant is lower compared to E2.

The concentration at steady-state C_{fss} was determined as described next. C_{fss} depends on the mass adsorbed and is obtained by mass balance of the feed solution in recirculation mode given by equation (8),

$$V_{feed} C_f(0) = V_{feed} C_{fss} + M_{ads} \quad (8)$$

where V_{feed} is the volume of the feed solution (L), M_{ads} is the total mass adsorbed (ng) at steady state. If the total mass adsorbed can be determined then C_{fss} will be known by applying equation (8). In the previous section it was concluded that the total mass adsorbed is dependent on $C_m(0)$ and in consequence $C_m(0)$ is the key parameter to predict adsorption.

The total mass adsorbed for any experimental hydrodynamic condition of pressure and Re_h number is predicted using the relationship between the total mass adsorbed and $C_m(0)$ obtained from the filtration isotherm experiments (Figure 4). For the filtration isotherm experiments, $C_m(0)$ is calculated according to equation (3) and plotted against the total mass adsorbed as shown in Figure

6 where a linear relationship is obtained. The higher the affinity of the compound with the membrane, the higher the slope of the linear isotherm will be. This is indeed the case with E1 compared to E2. For non-linear isotherms such as Freundlich or Langmuir, a non-linear relationship would have to be used.

[FIGURE 6]

For experiments of varying pressure and Re_h , $C_m(0)$ is calculated according to equation (3) and the total mass adsorbed is predicted using the linear relationship from Figure 6. With the predicted total mass adsorbed and equation (8), C_{fss} is obtained and used in equation (7).

Figure 7 and Figure 8 show the good prediction and validation of the developed model by applying equation (7) to the feed concentration with varying Re_h and pressure for both E1 and E2. Once the transient feed concentration is predicted, the next step is to predict the transient permeate concentration.

4.2 Permeate concentration prediction

A model that allows prediction of the permeate concentration variation with time was developed below. Steinle-Darling *et al.* [27] showed that retention of adsorbing compounds follows the same type of exponential decay as the feed concentration and is given by equation (9), where $Retention(0)$ is the initial retention (100%), $Retention_{ss}$ is the retention once steady-state is reached, t is time (s) and b is a first order constant (s^{-1}).

$$Ret(t) = Retention_{ss} + (Retention(0) - Retention_{ss}) \cdot e^{-bt} \quad (9)$$

Using the definition of retention in equation (9) and after algebraic manipulation, equation (10) is obtained, where C_{pss} is the permeate concentration at steady-state ($ng.L^{-1}$).

$$C_p(t) = \frac{C_{pss}}{C_{fss}} (1 - e^{-bt}) C_f(t) \quad (10)$$

To determine the transient permeate concentration C_{pss}/C_{fss} , the parameter b and $C_f(t)$ are required. It was previously concluded that $Retention_{ss}$, and therefore C_{pss}/C_{fss} , depends on the initial polarisation modulus β . Since the isotherm experiments have a constant β , and therefore a constant $Retention_{ss}$ (Figure 4), the isotherm data cannot be used to determine this ratio. Experiments with varying β were therefore used (Figure 9).

When β is plotted against C_{pss}/C_{fss} , a linear relationship is obtained for both hormones as shown in Figure 9. Once β is calculated for different conditions of pressure and Re_h numbers this relationship can subsequently be used to predict C_{pss}/C_{fss} , in much the same way as was done for the feed concentration prediction.

[FIGURE 7]

[FIGURE 8]

Constant b was determined by fitting equation (10) to the filtration isotherm experiments using an optimization method (Solver, Microsoft Excel). The parameter b obtained was $7.2 \times 10^{-4} s^{-1}$ for E2 and $2.0 \times 10^{-4} s^{-1}$ for E1. Hormone E1 has a lower first order constant because adsorption, and therefore feed and permeate concentration, take longer to reach steady-state compared to E2.

Figure 7 and Figure 8 show very good prediction and validation quality of the developed model by applying equation (10) for both E1 and E2 following the described method for different conditions of pressure and Re_h .

[FIGURE 9]

While transient permeate concentration is well predicted with this model, in the low pressure range (3 to 5 bar) for E1 and E2 and high Re_h number (998) for E1 the prediction did not fit the experimental results as well (data not shown). Concentration polarisation is not very pronounced at

these conditions. In fact the amount adsorbed and the Retention_{ss} for these three conditions are similar to what is obtained with a Re_h number in the transient regime (Re_h=1450), where polarisation is minimised (Figure 2 and Figure 3). Therefore using the relationship of Figure 6 with C_m(0) is prone to overestimate the predicted mass adsorbed. If the boundary condition C_f(0) is used instead of C_m(0) in Figure 6, meaning the concentration at the membrane surface is the same as the bulk and therefore no polarisation is considered, the prediction is more accurate (Figure 7 D and Figure 8 A and B).

The transient permeate trend provides information on the transport mechanisms of hormones. Since adsorption for E1 is much higher than for E2, the permeate concentration transient response is slower and takes longer to reach steady-state. Because more is adsorbed inside the membrane, it takes longer to obtain a breakthrough curve. Due to the higher sorption for E1 compared to E2 this is more emphasized for E1. Compounds that sorb in high quantities onto the membrane have a very low permeate concentration for a long time [27], sometimes giving 100% retention for the initial stages of the filtration (first 8 hours).

The lower the concentration at the membrane surface (low pressures and high Re_h numbers, the higher is retention and the slower is the breakthrough curve. This is because there is less driving force for the compound to permeate through and therefore less adsorption on the membrane.

5 Conclusions

Trace contaminant adsorption onto NF membranes has been shown to occur and the retentions obtained are lower than expected when only steric interactions are considered. This study elucidated the mechanisms that affect hormone adsorption and retention by NF membranes as far as surface hydrodynamics is concerned. Concentration polarisation, *i.e.* the initial concentration at the membrane surface was found to govern adsorption. For example, for a higher pressure or lower Re_h numbers, the initial concentration at the membrane surface increased, leading to an increase in the hormone mass adsorbed and decrease in retention. Adsorption was therefore found to be governed by the initial concentration at the membrane surface whilst retention was found to be governed by the initial polarisation modulus. The results of this work alert for the need in specifying very well the filtration conditions used in future studies since these affect the removal of trace contaminants.

These results further contribute to the understanding of hormone removal in spiral-wound modules, since these are subjected to the same hydrodynamic conditions as the ones in this study. The transient feed and permeate concentration can be estimated by the developed model, which makes recourse exclusively to hydrodynamic conditions and is therefore applicable to bench-scale and full-scale.

The ability to predict the permeate concentration for an adsorbing compound and understanding the fundamental mechanisms involved in their removal contributes to the minimisation of trials needed to control for the performance of a certain membrane. Furthermore, it also contributes to the design of more efficient membranes for micropollutant removal capable of either avoiding or even enhancing the occurrence of adsorption. In fact, membrane characteristics such as materials and pore radius are expected to affect hormone sorption and retention and therefore further work is necessary to add membrane parameters to the model.

Acknowledgements

Studentship of Andrea Semião was funded by the University of Edinburgh. Dr. Don Glass, Steve Gourlay and Bridgeen McCloskey are thanked for their help in obtaining the diaphragm pump and backpressure regulator. Jef Karn (Hydracell) is acknowledged for the diaphragm pump modifications, Dow Filmtec for providing the NF270 membrane, Annalisa de Munari for the Zeta Potential measurements at Imperial College, London and Helfrid Rossiter for the proof reading of the final document. Prof. Elimelech (Yale University) is thanked for the useful discussions.

References

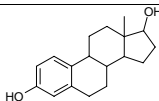
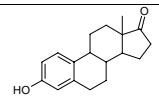
- [1] A.L. Batt, M.S. Kostich, J.M. Lazorchak, Analysis of ecologically relevant pharmaceuticals in wastewater and surface water using selective solid-phase extraction and UPLC-MS/MS, *Anal. Chem.*, 80 (2008) 5021-5030.
- [2] M. Rabet, A. Togola, F. Brissaud, J.-L. Seidel, H. Budzinski, F. Elbaz-Poulichet, Consequences of treated water recycling as regards pharmaceuticals and drugs in surface and ground waters of a medium-sized mediterranean catchment, *Environ. Sci. Technol.*, 40 (2006) 5282-5288.
- [3] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: a national reconnaissance, *Environ. Sci. Technol.*, 36 (2002) 1202-1211.
- [4] R.J. Williams, A.C. Johnson, J.J.L. Smith, R. Kanda, Steroid estrogens profiles along river stretches arising from sewage treatment works discharges, *Environ. Sci. Technol.*, 37 (2003) 1744-1750.
- [5] J.M. Smeets, I. van Holsteijn, J.P. Giesy, W. Seinen, M. van den Berg, Estrogenic potencies of several environmental pollutants, as determined by vitellogenin induction in a carp hepatocyte assay, *Toxicol Sci.*, 50 (1999) 206-213.
- [6] S. Jobling, J.P. Sumpter, Detergent components in sewage effluent are weakly oestrogenic to fish: An in vitro study using rainbow trout (*Oncorhynchus mykiss*) hepatocytes, *Aquat. Toxicol.*, 27 (1993) 361-372.
- [7] C.D. Metcalfe, T.L. Metcalfe, Y. Kiparissis, B.G. Koenig, C. Khan, R.J. Hughes, T.R. Croley, R.E. March, T. Potter, Estrogenic potency of chemicals detected in sewage treatment plant effluents as determined by in vivo assays with Japanese medaka (*Oryzias latipes*), *Environ. Toxicol. Chem.*, 20 (2001) 297-308.
- [8] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters, *Water Res.*, 41 (2007) 1013-1021.
- [9] C. Baronti, R. Curini, G. D'Ascenzo, A. Di Corcia, A. Gentili, R. Samperi, Monitoring natural and synthetic estrogens at activated sludge sewage treatment plants and in a receiving river water, *Environ. Sci. Technol.*, 34 (2000) 5059-5066.
- [10] D.M. Fry, Reproductive effects in birds exposed to pesticides and industrial chemicals, *Environ. Health Perspect.*, 103 (1995) 165-171.
- [11] J.P. Sumpter, Endocrine disruptors in the aquatic environment: an overview, *Acta Hydrochim. Hydrobiol.*, 33 (2005) 9-16.
- [12] S.A. Ahmed, The immune system as a potential target for environmental estrogens (endocrine disruptors): a new emerging field, *TOXICOLOGY*, 150 (2000) 191-206.
- [13] H. Inadera, The immune system as a target for environmental chemicals: xenoestrogens and other compounds, *Toxicology Letters*, 164 (2006) 191-206.
- [14] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Removal of natural hormones by nanofiltration membranes: measurement, modeling, and mechanisms, *Environ. Sci. Technol.*, 38 (2004) 1888-1896.
- [15] A.I. Schäfer, I. Akanyeti, A.J.C. Semião, Micropollutant sorption to membrane polymers: a review of mechanisms for estrogens, *Adv Colloid Interfac.*, doi:10.1016/j.cis.2010.09.006 (2010).
- [16] I. Koyuncu, O.A. Arkan, M.R. Wiesner, C. Rice, Removal of hormones and antibiotics by nanofiltration membranes, *J. Membr. Sci.*, 309 (2008) 94-101.

- [17] Y. Kiso, Y. Nishimura, T. Kitao, K. Nishimura, Rejection properties of non-phenylic pesticides with nanofiltration membranes, *J. Membr. Sci.*, 171 (2000) 229-237.
- [18] K. Kimura, S. Toshima, G. Amy, Y. Watanabe, Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes, *J. Membr. Sci.*, 245 (2004) 71-78.
- [19] K. Kimura, G. Amy, J.E. Drewes, T. Heberer, T.-U. Kim, Y. Watanabe, Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes, *J. Membr. Sci.*, 227 (2003) 113-121.
- [20] A.I. Schäfer, L.D. Nghiem, T.D. Waite, Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis, *Environ. Sci. Technol.*, 37 (2003) 182-188.
- [21] H.Y. Ng, M. Elimelech, Influence of colloidal fouling on rejection of trace organic contaminants by reverse osmosis, *J. Membr. Sci.*, 244 (2004) 215.
- [22] L.D. Nghiem, D. Vogel, S. Khan, Characterising humic acid fouling of nanofiltration membranes using bisphenol A as a molecular indicator, *Water Res.*, 42 (2008) 4049-4058.
- [23] W. Pronk, H. Palmquist, M. Biebow, M. Boller, Nanofiltration for the separation of pharmaceuticals from nutrients in source-separated urine, *Water Res.*, 40 (2006) 1405-1412.
- [24] Y. Zhang, C. Causserand, P. Aimar, J.P. Cravedi, Removal of bisphenol A by a nanofiltration membrane in view of drinking water production, *Water Res.*, 40 (2006) 3793-3799.
- [25] K. Kimura, G. Amy, J. Drewes, Y. Watanabe, Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact leading to overestimation of rejection, *J. Membr. Sci.*, 221 (2003) 89-101.
- [26] A.J.C. Semiao, A.I. Schäfer, Xenobiotics Removal by Membrane Technology: An Overview, in: D. Fatta-Kassinos, K. Bester, K. Kummerer (Eds.) *Xenobiotics in the urban water cycle: mass flows, environmental processes, mitigation and treatment strategies*, Springer Netherlands, 2010, pp. 307-338.
- [27] E. Steinle-Darling, E. Litwiller, M. Reinhard, Effects of sorption on the rejection of trace organic contaminants during nanofiltration, *Environ. Sci. Technol.*, 44 (2010) 2592-2598.
- [28] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Nanofiltration of hormone mimicking trace organic contaminants, *Sep. Sci. Technol.*, 40 (2005) 2633-2649.
- [29] K.M. Agbekodo, B. Legube, S. Dard, Atrazine and simazine removal mechanisms by nanofiltration: influence of natural organic matter concentration, *Water Res.*, 30 (1996) 2535-2542.
- [30] L.D. Nghiem, A.I. Schäfer, Critical risk points of nanofiltration and reverse osmosis processes in water recycling applications, *Desalination*, 187 (2006) 303-312.
- [31] V. Yangali-Quintanilla, A. Sadmani, M. McConville, M. Kennedy, G. Amy, A QSAR model for predicting rejection of emerging contaminants (pharmaceuticals, endocrine disruptors) by nanofiltration membranes, *Water Res.*, 44 (2010) 373-384.
- [32] A.R.D. Verliefde, E.R. Cornelissen, S.G.J. Heijman, E.M.V. Hoek, G.L. Amy, B.V.d. Bruggen, J.C. van Dijk, Influence of solute-membrane affinity on rejection of uncharged organic solutes by nanofiltration membranes, *Environ. Sci. Technol.*, 43 (2009) 2400-2406.
- [33] J.Y. Hu, X. Jin, S.L. Ong, Rejection of estrone by nanofiltration: influence of solution chemistry, *J. Membr. Sci.*, 302 (2007) 188-196.
- [34] E.R. Cornelissen, J. Verdouw, A.J. Gijsbertsen-Abrahamse, J.A.M.H. Hofman, A nanofiltration retention model for trace contaminants in drinking water sources, *Desalination*, 178 (2005) 179-192.
- [35] E.A. McCallum, H. Hyung, T.A. Do, C.-H. Huang, J.-H. Kim, Adsorption, desorption, and steady-state removal of 17 β -estradiol by nanofiltration membranes, *J. Membr. Sci.*, 319 (2008) 38-43.
- [36] A.R.D. Verliefde, S.G.J. Heijman, E.R. Cornelissen, G. Amy, B. Van der Bruggen, J.C. van Dijk, Influence of electrostatic interactions on the rejection with NF and assessment of the removal efficiency during NF/GAC treatment of pharmaceutically active compounds in surface water, *Water Res.*, 41 (2007) 3227-3240.
- [37] P. Xu, J.E. Drewes, C. Bellona, G. Amy, T.-U. Kim, M. Adam, T. Heberer, Rejection of emerging organic micropollutants in nanofiltration/reverse osmosis membrane applications, *Water Environ. Res.*, 77 (2005) 40-48.
- [38] L.D. Nghiem, A.I. Schäfer, Adsorption and transport of trace contaminant estrone in NF/RO membranes, *Environ. Eng. Sci.*, 19 (2002) 441-451.
- [39] H.Y. Ng, M. Elimelech, Influence of colloidal fouling on rejection of trace organic contaminants by reverse osmosis, *J. Membr. Sci.*, 244 (2004) 215-226.
- [40] L.D. Nghiem, A. Manis, K. Soldenhoff, A.I. Schäfer, Estrogenic hormone removal from wastewater using NF/RO membranes, *J. Membr. Sci.*, 242 (2004) 37-45.
- [41] T. Thorsen, H. Fløgstad, (2006), Nanofiltration in drinking water treatment, Techneau, <http://www.techneau.org/fileadmin/files/Publications/Publications/Deliverables/D5.3.4b.pdf>
- [42] G. Schock, A. Miquel, Mass transfer and pressure loss in spiral wound modules, *Desalination*, 64 (1987) 339-352.
- [43] K. Boussu, J.D. Baerdemaeker, C. Dauwe, M. Weber, K. G. Lynn, D. Depla, S. Aldea, I. F. J. Vankelecom, V. Carlo, B.V.d. Bruggen, Physico-chemical characterization of nanofiltration membranes, *ChemPhysChem*, 8 (2007) 370-379.
- [44] M. Mulder, *Basic Principles of Membrane Technology*, 2nd Edition ed., Kluwer Academic Publishers, Dordrecht, 1996.
- [45] S. Lee, G. Amy, J. Cho, Applicability of Sherwood correlations for natural organic matter (NOM) transport in nanofiltration (NF) membranes, *J. Membr. Sci.*, 240 (2004) 49-65.
- [46] E. Worch, Eine neue Gleichung zur Berechnung von Diffusionskoeffizienten gelöster Stoffe, vom Wasser, 81 (1993) 289-297.
- [47] P.A. Neale, B.I. Escher, A.I. Schäfer, pH dependence of steroid hormone-organic matter interactions at environmental concentrations, *Sci. Total Environ.*, 407 (2009) 1164-1173.
- [48] T. Fukuhara, S. Iwasaki, M. Kawashima, O. Shinohara, I. Abe, Adsorbability of estrone and 17 β -estradiol in water onto activated carbon, *Water Res.*, 40 (2006) 241-248.
- [49] M. Fuerhacker, A. Dürauer, A. Jungbauer, Adsorption isotherms of 17 β -estradiol on granular activated carbon (GAC), *Chemosphere*, 44 (2001) 1573-1579.
- [50] J.H. Kwon, H. Liljestrand, L.E. Katz, Partitioning of moderately hydrophobic endocrine disruptors between water and synthetic membrane vesicles, *Environ. Toxicol. Chem.*, 25 (2006) 1984-1992.
- [51] C. Hansch, A. Leo, D. Hoekman, *Exploring QSAR: hydrophobic, electronic, and steric constants*, ed., American Chemical Society, Washington, DC., 1995.
- [52] C. Kubli-Garfias, Comparative study of the electronic structure of estradiol, epiestradiol and estrone by ab initio theory, *J. Mol. Struct. THEOCHEM*, 452 (1998) 175-183.
- [53] C.W. Lim, S.-i. Fujiwara, F. Yamashita, M. Hashida, Prediction of human skin permeability using a combination of molecular orbital calculations and artificial neural network, *BIOL PHARM BULL.*, 25 (2002) 361-366.
- [54] A. Bhandari, Surampalli, R. Y., Adams, C. D., Champagne, P., Ong, S. K., Tyagi, R. D. & Zhang, T. C., *Contaminants of Emerging Environmental Concern*, ed., ASCE, 2009.

Table 1 NF 270 membrane characteristics

Isoelectric Point	Water Permeability (L.h ⁻¹ .m ⁻² .bar ⁻¹)	NaCl Rejection (%) (0.1 M, 10 bar)	MWCO (Da)
pH 3.6	17.0 ± 0.8	52 ± 0.06	180 ± 20

Table 2 Properties for natural hormones estradiol (E2) and estrone (E1).

Compound	Molecular Formula	CAS No.	Mol Structure	MW (g/mol)	Solubility in water (mg/L)	pK _a	Log K _{ow}	Dipole moment (Debye)
17-β Estradiol (E2)	C ₁₈ H ₂₄ O ₂	50-28-2		272	3.6, 82 ^{a,c,h}	10.23 ^b	4.01 ^d	2.2 ^e , 2.7 ^g
Estrone (E1)	C ₁₈ H ₂₂ O ₂	53-16-7		270	13, 147 ^{c,f,h}	10.34 ^b	3.13 ^d	2.1 ^e , 3.4 ^g

^a [18], ^b [50], ^c [40], ^d [51], ^e [52], ^f [20], ^g [53], ^h [54]

Table 3 Comparison between the E1 and E2 mass adsorbed and retention for different pressure and Reh numbers combinations (11 bar and a Reh number of 1000 with the experiment at 8 bar and Reh number of 427)

Hormone	Experiment	C _m (0) (ng.L ⁻¹)	β	Mass Adsorbed (ng.cm ⁻²)	Retention (%)
E1	11 bar, Reh=1000	125	1.25	1.3	75
	8 bar, Reh=427	125	1.25	1.3	73
E2	11 bar, Reh=1000	125	1.25	0.6	71
	8 bar, Reh=427	125	1.25	0.6	70

List of Figures

Figure 1 Cross-flow system piping and instrumentation diagram

Figure 2 Reynolds number (Re_h) influence on (A) E1 and (B) E2 steady-state retention (Retention_{ss}) and total mass adsorbed (Mass Ads.) and (C) polarisation modulus β (C_{feed}(0)=100 ng.L⁻¹, P=11 bar, T=24°C, pH 7). The approximate region of change from laminar to transition regime is identified in the figure

Figure 3 Pressure influence on (A) E1 and (B) E2 steady-state retention (Retention_{ss}) and total mass adsorbed (Mass Ads.) and (C) polarisation modulus β (Re_h=427, C_{feed initial}=100 ng/L, T=24°C, pH 7)

Figure 4 E1 and E2 sorption isotherm in filtration and static mode (E2) and retention at steady state as a function of equilibrium feed concentration (cross-flow filtration conditions: Re_h=427, P=11 bar, T=24°C, pH 7; Static conditions: T=24°C, 200 rpm). The total mass adsorbed is given by Mass Ads.

Figure 5 Normalized permeate transient flux for the E2 isotherm experiments in filtration mode (cross-flow filtration conditions: Re_h=427, P=11 bar, T=24°C, pH 7, pure water flux: J₀=17 L/h.m².bar)

Figure 6 E1 and E2 initial concentration at the membrane surface (C_m(0)) as a function of total mass adsorbed (Mass Ads.) for the filtration isotherm experiments

Figure 7 Experimental and predicted dimensionless feed and permeate concentration (transient feed and permeate concentration divided by initial feed concentration) for several Reynolds numbers (Re_h) (A) 570, (B) 698, (C) 855 and (D) 998 for E1 and E2 (C_{feed initial} (t=0)=100 ng/L, T=24°C, pH 7, P=11 bar)

Figure 8 Experimental and predicted dimensionless feed and permeate concentration for several pressures (A) 3 bar, (B) 5 bar, (C) 8 bar, (D) 11 bar and (E) 17 bar for E1 and E2 (C_{feed initial} (t=0)=100 ng/L, T=24°C, pH 7, Re_h=427)

Figure 9 Polarisation modulus β as a function of C_{p ss}/C_{f ss} for E2 and E1 (Re_h=1450, C_{feed}=100 ng/L, P=11 bar; Re_h=427, C_{feed}=100 ng/L, P=11 bar; Re_h=427, C_{feed}=100 ng/L, P=15 bar)

FIGURE 1

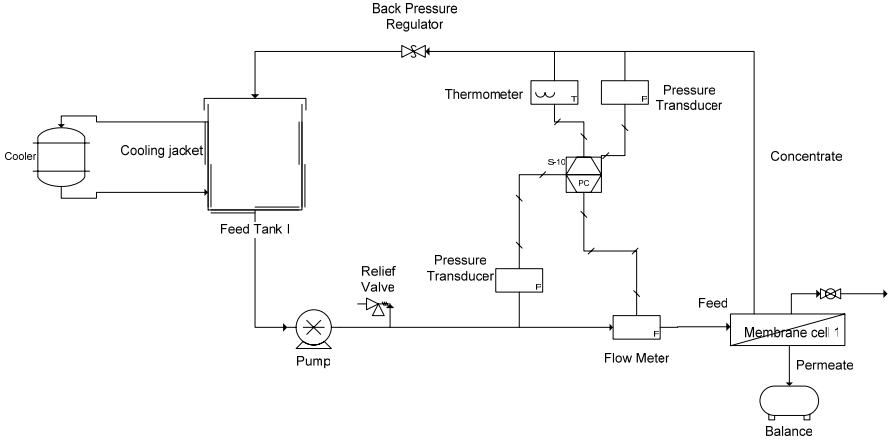


FIGURE 2

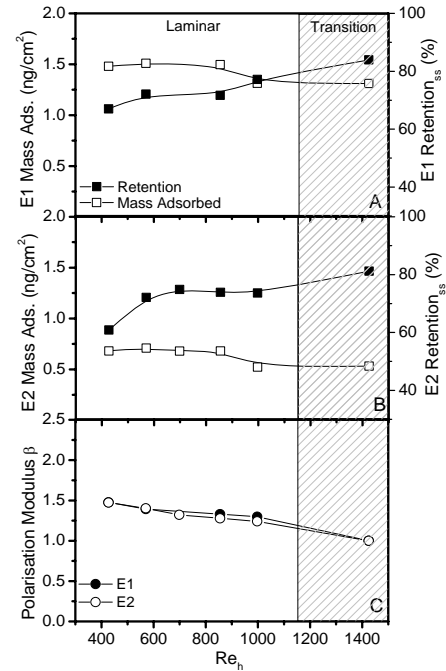


FIGURE 3

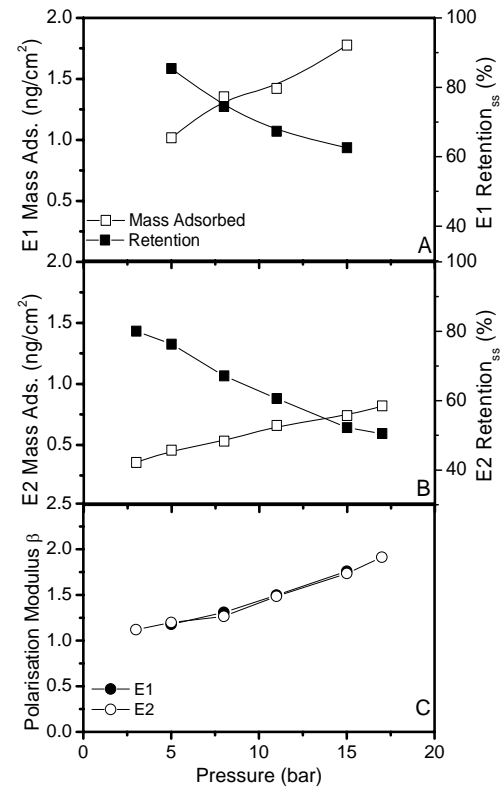


FIGURE 4

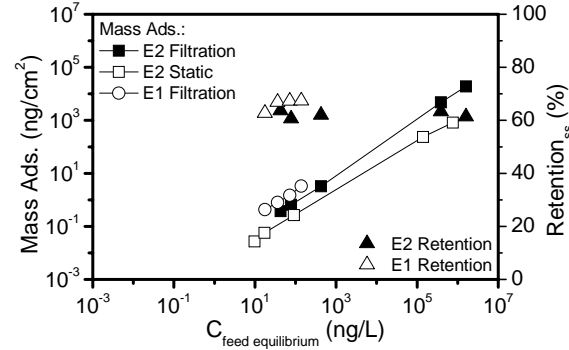


FIGURE 5

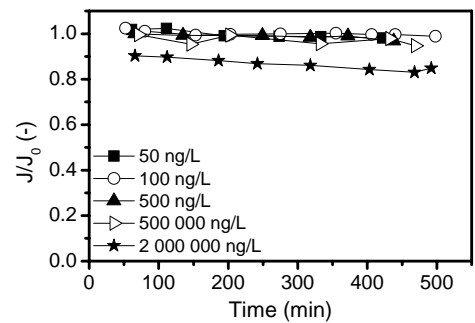


FIGURE 6

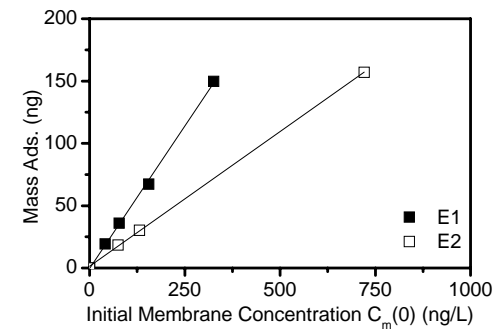


FIGURE 7

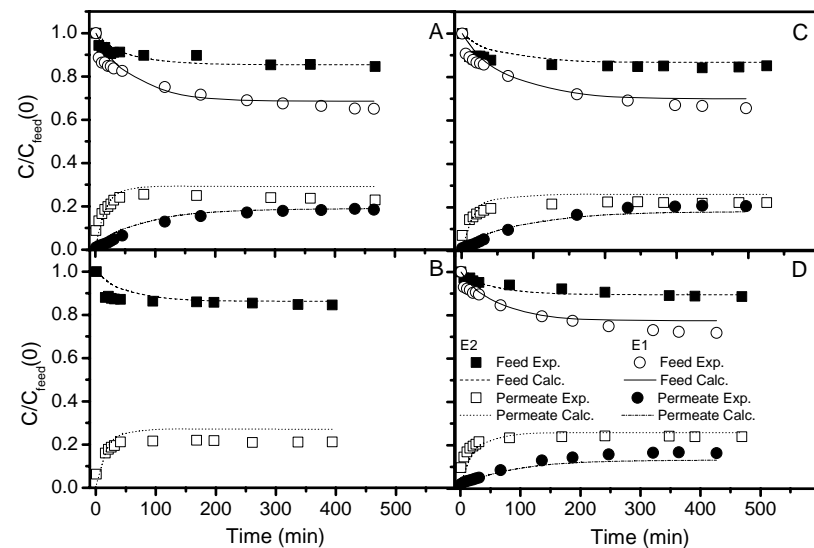


FIGURE 8

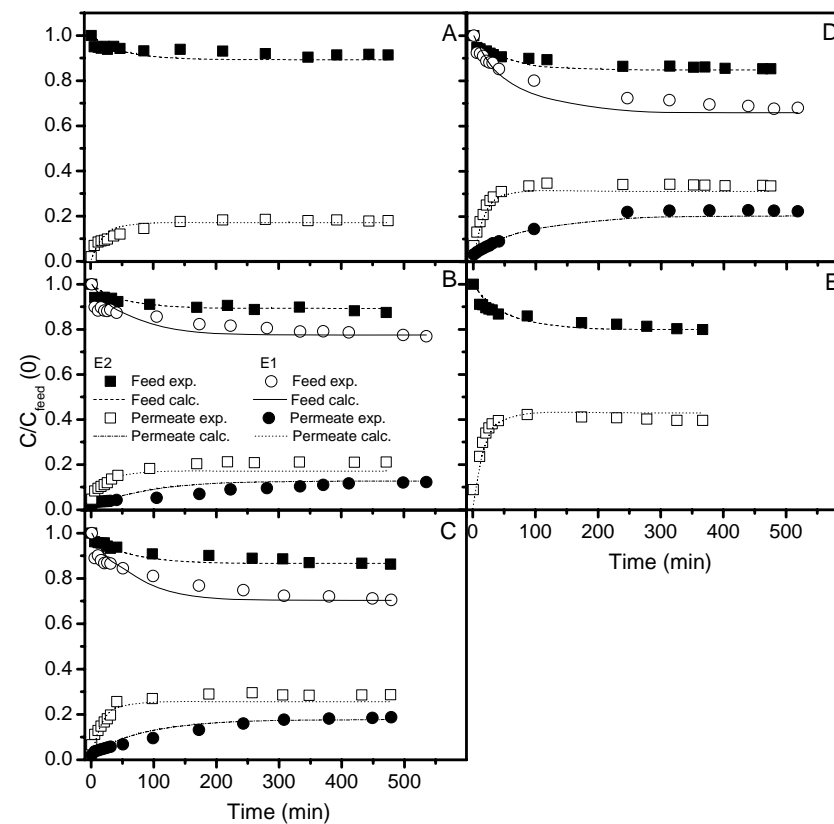


FIGURE 9

